Chapter 8. Evaluating Environmental Performance During Process Synthesis

by
David T. Allen, David R. Shonnard, and Scott Prothero

The design of chemical processes proceeds through a series of steps, beginning with the specification of the input-output structure of the process and concluding with a fully specified flowsheet. Traditionally, environmental performance has only been evaluated at the final design stages, when the process is fully specified. This chapter presents methodologies that can be applied at a variety of stages in the design process, allowing the process engineer more flexibility in choosing design options that improve environmental performance.

The search for "greener chemistry", described in the previous chapter, can lead to many exciting developments. New, simpler synthesis pathways could be discovered for complex chemical products resulting in a process that generates less toxic byproducts and lowers the overall risk associated with the process. Toxic intermediates used in the synthesis of commodity chemicals might be eliminated. Benign solvents might replace more environmentally hazardous materials. However, these developments will involve new chemical processes as well as Green Chemistry.

The art and craft of creating chemical processes is the topic of a number of excellent textbooks (see, for example, Douglas, 1988). A fundamental theme that arises in each of these texts is that the design process proceeds through a series of steps each involving an evaluation of the associated environmental impacts. At the earliest stages of a design, only the most basic features of a process are proposed. These include the raw materials and chemical pathway to be used, as well as the overall material balances for the major products, by-products and raw materials. Large numbers of design alternatives are screened at this early design stage, and the screening tools used to evaluate the alternatives must be able to handle efficiently large numbers of alternative design concepts. As design concepts are screened, a select few might merit further study. Preliminary designs for the major pieces of equipment to be used in the process need to be specified for the design options that merit further study. Material flows for both major and minor by-products are estimated. Rough emission estimates, based on analogous processes, might be considered. At this development stage, where fewer design alternatives are considered, more effort can be expended in evaluating each design alternative, and more information is available to perform the evaluation. If a design alternative appears attractive at this stage, a small-scale pilot plant of the process might be constructed and a detailed process flow sheet for a full-scale process might be constructed. Very few new design ideas reach this stage, and the investments made in evaluating design alternatives at this level are substantial. Therefore, process evaluation and screening tools can be quite sophisticated.

Traditionally, evaluations of environmental performance have been restricted to the last stages of this engineering design process, when most of the critical design decisions have already been made. A better approach would be to evaluate environmental performance at each step in the design process. This would require, however, a hierarchy of tools for evaluating environmental performance. Tools that can be efficiently applied to large numbers of alternatives, using limited information, are necessary for evaluating environmental performance at the earliest design stages. More detailed tools could be employed at the development stages, where potential emissions and wastes have been identified. Finally, detailed environmental impact assessments would be performed as a process nears implementation.

This chapter and Chapter 11 present a hierarchy of tools for evaluating the environmental performance of chemical processes. Three tiers of environmental performance tools will be presented. The first tier of tools, presented in Section 8.2, is appropriate for situations where only chemical structures and the input-output structure of a process is known. Section 8.3 describes a second tier of tools, which is appropriate for evaluating the environmental performance of preliminary process designs. This tier includes tools for estimating wastes and emissions. Finally, Section 8.4 introduces methods for the detailed evaluation of flowsheet alternatives, which will be discussed in Chapter 11.

Chapter 8 Example Problem

Example 8.3-2

A company wants to sell a newly-developed substitute for dimethylsulfoxide (DMSO) in pharmaceutical manufacturing. 300,000 lb/yr of this new "drop-in" substitute for DMSO could be sold to two customer pharmaceutical plants who will each purchase the same volume of the substitute. US EPA requires submission of a Premanufacture Notice (PMN) for this new chemical. The PMN form requests estimated releases to all media from downstream customers (the pharmaceutical plants) in units of kg/day. Generate these estimates.

Solution

Assume that the physical/chemical properties of the new chemical match the properties of DMSO very closely. The customer plants are reluctant to divulge proprietary process information, but one detail they give is that the facilities operate five days each week for 50 weeks of the year. Based on a search of several release estimation resources you find that the US EPA document entitled "Compilation of Air Pollutant Emission Factors" (often referred to as "AP-42") contains emission factors for DMSO for the pharmaceutical industry. The reference table notes that these data are based on an industry survey. Because both the release-affecting properties and the industrial use of the new chemical and DMSO are so similar, you have concluded that these DMSO emission factors are suitable surrogates for estimating releases of your company's new chemical. The AP-42 DMSO emission factors for the pharmaceutical industry are 1% to air emissions, 28% to sewer, and 71% to incineration (AP-42, Section 6.13). You contacted the potential customers, and they acknowledged that these AP-42 emission factors reasonably represent their facilities.

Calculation: First calculate the amount used per day at each site, then apply the emission factors to calculate the release to the media.

1. Daily average amount (mass) used at each site =
   300,000 lb/yr / 2.20 kg/lb / 2 sites / (5 days/week x 50 weeks/yr) = 273 kg/day
2. Partition the daily use amount to the media based on the emission factors:
   release to air = 1% of 273 kg/day = 2.7 kg/day
   release to water = 28% of 273 kg/day = 76 kg/day
   release to incineration = 71% of 273 kg/day = 194 kg/day

Chapter 8 Sample Homework Problem

1. Compare the carbonylation of dinitrotoluene and the amine-phosgene routes for the production of toluene diisocyanate (TDI) using a Tier 1 economic and environmental performance evaluation. The amine- phosgene route involves the reaction of phosgene with toluenediamine in a chlorobenzene solvent. The carbonylation route has been demonstrated in laboratories, but is not presently a commercial technology. Data from the patent literature (see the Green Chemistry Expert System referenced in Chapter 7) indicate that the reaction of 2,4 dinitrotoluene with carbon monoxide occurs over a mixed oxide catalyst. Conversion approaches 100% with selectivity to the desired product ranging from 70 - 99%. Laboratory data indicate that the reaction can be performed in a chlorobenzene and pyridine solvent. Approximate stoichiometric data, based on the patent data, are given in the Table below. Compare the carbonylation of nitrobenzene and the amine phosgene routes for the production of methylene diphenylene diisocyanate (MDI).

Amine - phosgene route:

$$C_6H_3(CH_3)(NH_2)_2 + 2\ COCl_2 \Rightarrow\ C_6H_3(CH_3)(-N=C=O)_2\ + 4\ HCl$$

Carbonylation of nitrobenzene:

$$C_6H_3(CH_3)(NO_2)_2 + 6\ CO \Rightarrow C_6H_3(CH_3)(-N=C=O)_2 + 4\ CO_2$$

Compound	*Pounds produced or pounds of raw material required per pound of MDI**	*Cost ($/lb)***	*PEL ($\mu g/m^3$)*	*Overall inhalation toxicity factor*	*Overall oral toxicity factor*
Amine - phosgene route					
toluene diamine	-0.76	0.576	0.1 (est.)	NA	NA
chlorobenzene	-0.01	0.550	350	100	100
hydrochloric acid	0.4 (est.)	0.027	7	100	100
phosgene	-1.26	0.610	0.4	NA	NA
TDI	1.00	1.340	0.14	100,000	100

Carbonylation route					
dinitrotoluene	1.04 (est.)	0.365	1.5	1,000	1,000
carbon monoxide	1.0 (est.)	0.040	55	NA	NA
TDI	1.00	1.340	0.14	100,000	100
carbon dioxide	1.0 (est.)	-	9000	NA	NA

* A negative stoichiometric index indicates that a material is consumed; a positive index indicates that it is produced in the reaction

**Chang, 1996